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FIELD INFRARED METHOD TO DISCRIMINATE NATURAL SEEPS FROM NON-SE--ETC(U)
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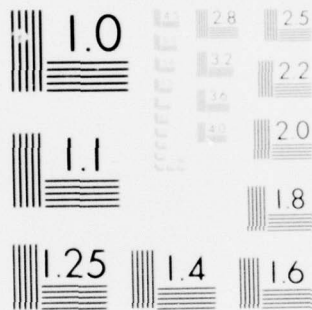
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Report No. CG-D-32-77

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FIELD INFRARED METHOD TO DISCRIMINATE NATURAL SEEPS
FROM NON-SEEPS (SANTA BARBARA, CALIFORNIA AREA)

DeLyle Eastwood and Douglas F. Grant
U.S. Coast Guard Research and Development Center
Avery Point
Groton, Connecticut 06340



December 1976

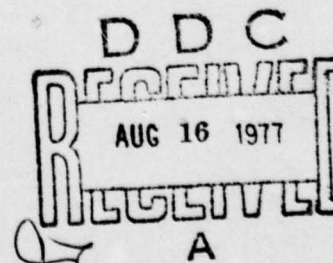
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<p>16. Abstract A field infrared method has been developed to distinguish oil due to natural seepage in the Santa Barbara (California) Channel region from closely similar oils derived from spills at offshore drilling platforms or from shipping accidents. Differences between seep and non-seep oils have been found to persist in weathering studies carried out in outdoor tanks for one week. This method involves simple infrared instrumentation and a minimum of sample preparation. It permits rapid on-site analysis without special training. The major differences between seep and non-seep oils appear in the comparison between the 13.8 μ and 13.5 μ peaks (for both weathered and unweathered oils) and in the carbonyl region at 5.85 μ (for unweathered oils only).</p> <p><i>MICROMETERS</i></p>		
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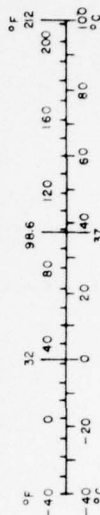
Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
AREA				
m ²	square inches	6.5	square centimeters	cm ²
ft ²	square feet	0.09	square meters	m ²
yd ²	square yards	0.8	square meters	m ²
mi ²	square miles	2.6	square kilometers	km ²
	acres	0.4	hectares	ha
MASS (weight)				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
VOLUME				
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.96	liters	l
gal	gallons	3.8	liters	l
ft ³	cubic feet	0.03	cubic meters	m ³
yd ³	cubic yards	0.76	cubic meters	m ³
TEMPERATURE (exact)				
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in x 2.54 exactly. For other exact conversions and more data, see tables, see also Metric, Page 286.
Units of Weights and Measures, Price \$2.25, SO Catalog No. C13-110-286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
AREA				
cm ²	square centimeters	0.16	square inches	in ²
m ²	square meters	1.2	square yards	yd ²
km ²	square kilometers	0.4	square miles	mi ²
ha	hectares (10,000 m ²)	2.5	acres	
MASS (weight)				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
VOLUME				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m ³	cubic meters	35	cubic feet	ft ³
m ³	cubic meters	1.3	cubic yards	yd ³
TEMPERATURE (exact)				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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1.0 INTRODUCTION

1.1 Scope. The purpose of this project was to develop a relatively simple field method to distinguish between natural seeps and production oils (or other spill sources) in the Santa Barbara, California area. It has also proved useful to classify oils by type, and displayed potential for matching a spilled sample to a suspect source.

1.2 Application. The method can be applied to any neat oil, waterborne oil or oil-soaked material (following extraction, if necessary).

1.3 Infrared Method Applied to Oil Analysis. The infrared absorption spectrum of a petroleum oil is the sum of the absorptions of all the infrared active vibrations of all the component molecules in this highly complex mixture. All vibrations are infrared-active if they result in a change in electric dipole moment (displacement of electric charge) within the molecule. For hydrocarbons, this means the asymmetric vibrations. Vibrations include bending, stretching and twisting motions of the molecule as a whole or of individual bonds. Certain peaks may be found to have mainly aromatic or mainly aliphatic character, whereas other peaks will be found to represent the stretching of a particular type of bond such as carbonyl ($C=O$), or hydroxyl (OH). Therefore, the infrared spectrum gives us a good handle on the overall composition of the oil including components such as aliphatics, and the presence of certain contaminants if present in large enough concentration. Since oil is such a complex mixture, individual components of the oil are generally not determined.

Infrared spectroscopy is not a good method for studying trace contamination of the oil, especially if the contaminant absorbs in a region of general hydrocarbon absorption. Certain solvent contaminant peaks such as pentane, used in deasphalting or extraction procedures, may be present and may distort the underlying infrared envelope without being noticeable except to an experienced operator. Therefore, it is advisable to avoid adding solvents to the oil unless necessary. This is also the reason for evaporating off all organic solvents before filling the cell. Also, many inorganic compounds such as magnesium sulfate, used in sample preparation, also absorb in the infrared and may cause contamination peaks of which the operator must be aware. Finally, atmospheric absorption peaks may be noticed and changes in the spectral baseline may be caused by scratching and darkening of the cell windows, especially silver bromide ($AgBr$). The latter effects may be checked by running an empty cell baseline.

1.4 Description of Instrument. Figure 1 shows a schematic diagram of the single-beam instrument which is used for the field method because its ruggedness, low-cost and ease of operation outweighed the instrumental shortcomings over a double-beam spectrophotometer, for this field application. The source is a resistively-heated nichrome wire. A circular variable interference filter is used in combination with a slit to select a single narrow wavelength band from the source radiation. The selected wavelength bandpass is varied over the range 2.5-14.5 microns (in three steps) by rotating the filter.

A pyroelectric lithium tantalate detector is exposed to chopped radiation which has passed through the sample cell and the resulting signal is sensed as an alternating voltage across a large-value, parallel resistor. This detector is used because of its ruggedness and rapid response. It is not degraded by normal exposure to the atmosphere but must be protected from strong drafts when in use. The basic signal-to-noise ratio of the instrument is determined by the "Johnson noise" in the parallel resistor due to the random thermal motion of electric charges and by the intensity of radiation falling on the detector.

The specifications of the Miran I model 5649 are shown in Table 1.

1.5 Differences Between Single and Double-Beam Infrared Spectral Method

In modern infrared spectrophotometry, double-beam instruments are used almost exclusively. Consequently, not everyone is familiar with the distinctions between single and double-beam spectrophotometers. The major distinctive features of the single-beam instrument are outlined below.

For the single-beam method:

1.5.1 The instrument resolution is lower. This is a disadvantage in that some information is lost, but the important features of the infrared spectra are still observable.

1.5.2 The spectral baseline will be sloping rather than flat as for the double-beam instrument. Also, interferences due to atmospheric absorbances of CO_2 (4.25 μ) and H_2O (2.7 μ) may occur.

1.5.3 The gain is set with reference to a polystyrene standard. (For the double-beam spectrophotometer, the gain is adjusted at a fixed wavelength with the filled cell in place.) When using the single-beam instrument, it is important always to use the same Teflon spacer (for the sealed demountable cell) and/or the same Mini-cell windows, so that the relative absorbances can be compared directly, since small differences in cell thickness are not compensated by the calibration procedure. This

method has the advantage that relative absorbance differences among oils will be maintained. Therefore, relative API gravities ("weights") of oils can be compared by observing the absorbances at certain wavelengths (e.g., 7.5 μ).

1.5.4 The Miran instrument has a linear absorbance capability, in addition to the linear transmittance which is available in most double-beam instruments. The Miran has two absorbance ranges (0-1 and 1-2 Optical Density).

1.5.5 The Miran abscissa is linear in microns rather than wavenumbers as are most double-beam instruments. The Miran abscissa is divided into three segments because of the filter wheel construction.

2.0 SUMMARY OF METHOD

2.1 The neat, weathered or unweathered, petroleum crude or refined oil sample is first placed in either a sealed demountable cell with silver bromide (AgBr) windows and a 0.1 mm Teflon spacer or in a Wilks Mini-cell also with AgBr windows and a 0.1 mm pathlength. If the sample is known to contain water, additional sample preparation steps will be required.

The cell is then placed in the infrared analyzer and the infrared spectrum on the transmittance scale is scanned from 2.5 to 14.5 μ . Then, the spectrum is scanned from 8 to 11 μ on the (0-1 O.D.) or 1x linear absorbance scale and from 11 to 14.5 μ on the (1-2 O.D.) or 10x linear absorbance scale. Afterwards, spectra are analyzed by examining major spectral features or by using the overlay method. (See Section 3.)

3.0 INTERPRETATION

Discrimination between a natural seep and a production oil (crude) from the same geographical area (Santa Barbara, California) involves examination of two areas of the spectrum. The first region examined (5.85 μ) indicates the presence or absence of a carbonyl peak. If no carbonyl peak exists, the oil is an unweathered production oil. If a carbonyl peak is present, the oil is either a natural seep or a weathered production oil. After approximately two days of weathering, the distinction based on the carbonyl peak is lost. In this case, discrimination must be made by examining the 13.5 μ /13.8 μ peak ratio. This ratio is larger for more aromatic oils such as natural seeps. Natural seeps, although they lose some aromatic components on weathering, remain more aromatic than the production oils even after prolonged weathering. Discrimination between natural seep and closely similar (brown zone) production oils has been found possible for up to one week of weathering.

Natural seep oil samples were collected from the surface of the water, underwater and from the beaches. The non-seep oils were obtained from production wells in the same geographical areas as the seepage and from several different well depths corresponding to different geological zones. Samples examined in the present study included 41 production oils, 15 seep oils and 13 beach tar samples. Of the seep oils, 13 were from

surface oil slicks and two were underwater samples taken directly from the seeps, one from Coal Oil Point and the other from nearby Isla Vista. Since many of the reported seeps are only intermittently active, we were unable to collect as many different seep sources as we had originally planned. A sample of the Coal Oil Point natural seep collected underwater directly from the seep was selected as a comparison with the production oils because it was the largest and least weathered sample.

Figure 2 shows Miran spectra run on the transmittance scale in the spectral region from 8 to 4.5 μ . This figure compares three unweathered production oils from the Dos Cuadras field (labeled purple, brown and green) with a Coal Oil Point natural seep collected underwater. The carbonyl peak can be observed in the natural seep at 5.85 μ . At 7.5 μ , there are differences in the infrared absorbance which correspond approximately to the density or A.P.I. gravity of the oil studied.

For natural seep discrimination from production oils and/or spilled oils, all comparisons should initially be made by examining main spectral features or using spectral overlays, since the spectral distinctions are usually unambiguous. Standard spectra of known seeps and production oils (especially brown and green zone Dos Cuadras) should be kept on hand for comparison, and samples of known oils as standards should be kept on hand to run spectra for comparison at the same time as the unknown sample. It is possible to ratio peaks, quantitatively, by drawing slanted baselines from absorbance minimum to absorbance minimum. (Unfortunately, this baseline approach has uncertainties, although it is used by an ASTM method.) Since the Miran has good photometric accuracy, ± 0.5 percent, and since good overlays (better than 1% T) could be obtained using the precautions described in this discussion, the principal sources of error are in weathering and/or baseline determination (if peak ratios are to be used).

Figure 3 shows the same oils as in Figure 2 on absorbance scales of the Miran, 0-1 O.D. for the region from 11 μ to 8 μ and 1-2 O.D. for the region from 14.5 μ to 11 μ . The 13.5 μ /13.8 μ peak ratio is a rough indication of the relative aromatic/aliphatic content of the oil and the natural seep has the most aromatic character.

Weathering is an important part of the problem of distinguishing between seeps and non-seeps since often the oils do not wash ashore until they are extensively weathered. Figures 4 and 5 show weathering comparisons for a brown zone production oil (Dos Cuadras) unweathered and weathered three days on the transmittance and absorbance scales, respectively. Figure 6 shows a similar weathering comparison for a natural seep sample (Isla Vista) on the absorbance scales. These oils were weathered in outside troughs with circulating sea water and a water temperature of 20°C.

4.0 APPARATUS AND MATERIALS

4.1 Instrument

The basic instrument is the Wilks Miran I Infrared Analyzer, which is described in 1.4. The linear absorbance scales are required in the fingerprint region from 8-14.5 μ to obtain sufficient spectral detail for identification. The instrument is used with any compatible strip-chart recorder with time response < 1 second for full-scale deflection and 1 volt input.

Any other equivalent commercial infrared spectrophotometer (single- or double-beam) with similar photometric accuracy and resolution at least as high could be used with minor modifications to this procedure.

4.2 Cells and Windows

Sealed demountable cell with 0.1 mm Teflon spacer and AgBr windows or Wilks minicell with flat cover AgBr window and 0.1 mm cell depth AgBr window or RIIC disposable cell with AgCl windows and 0.1 mm cell thickness.

4.3 Auxiliary Equipment

Portable hood (for field work), hot plate for sample preparation, light box.

4.4 Expendable Materials

Expendables include: spectroquality solvents necessary for sample treatment (pentane) and for cleaning cells (toluene and hexane which are recommended for field use because of their relatively low toxicity), anhydrous magnesium sulfate for drying samples, standard 0.05 mm polystyrene film, chart paper, extra recorder pens, Pasteur pipets, micropipets, centrifuge tubes, Kimwipe or equivalent tissues and lens paper (non-silicone treated).

5.0 SPECTROSCOPIC PROCEDURES

5.1 Infrared Analyzer and Recorder

Refer to the instrument manual for information on operation, maintenance, specifications and troubleshooting.

5.1.1 Turn on instrument and recorder and warm up for 15 minutes.

5.1.2 Zero the strip-chart recorder.

5.1.3 Insert a standard 0.05 mm polystyrene film in the sample position.

5.1.4 Set Scale Expansion -1x (low gain setting)

Function switch - 100 % T

Time Constant - 0.25 sec. (Setting 1)

Slit Width - 0.5 mm

Filter Wheel - 3.34 microns

5.1.5 Adjust gain to read 0.90 transmission at 3.34 microns.

5.1.6 Close slit and remove film.

NOTE 1: Close slit when the instrument is not in use to prevent detector overload.

NOTE 2: Be careful not to alter the gain adjustment after it has been set against the polystyrene standard.

NOTE 3: Usually, the external detector/preamplifier unit is locked into a position corresponding to the maximum signal; however, if the unit has been packed, moved or severely jarred, it may be necessary to check the alignment of the external detector unit and reposition for maximum signal.

5.1.7 At least once a week run a spectrum of the polystyrene film to check the wavelength accuracy of the instrument. (See Figure 7.)

5.1.8 At least once a day run an empty cell blank to check the degree of atmospheric absorption due to water vapor (2.7μ) or carbon dioxide (4.25μ). At the same time, check for possible changes in spectral baseline due to scratching or darkening of the cell windows. (See Section 5.6).

5.2 Sample Analysis

5.2.1 Place the sample holder and cell in the sample position.

5.2.2 Open slit to 0.50 mm.

5.2.3 Set the filter wheel at 2.5 microns. Check that function switch is set at 100% T scale.

5.2.4 Engage scan motor on Miran and chart drive on recorder at the same time. Scan past 14.5 microns. Mark beginning and end of scan on the chart paper and indicate the wavelength values to which the marks correspond for each segment of the scan. Each segment is linear in microns. Close slit and disengage the scan and chart.

5.2.5 Change function switch to 1, linear absorbance scale (0-1 O.D.). Set the filter wheel at 8.0 microns. Open slit to 0.50 mm.

5.2.6 Engage scan and chart drive. At approximately 11 microns the pen will go off scale. At this point, change scale expansion to 10x (high gain setting), this corresponds to (1-2 O.D.) linear absorbance scale. Scan from 11 to beyond 14.5 microns. Close slit, disengage scan and chart; return scale expansion to 1x (low gain) and change range switch to 100% T scale.

5.3 Preparation of Sample

5.3.1 Pipet 2 ml of oil sample into a centrifuge tube.

5.3.2 Remove any visible water with a micropipet.

5.3.3 Place the centrifuge tube in 60°C water bath for 10 minutes. (For intermediate viscosity oils, use 35°C; for light oils, eliminate this step.)

5.3.4 Add 0.5 gram of anhydrous MgSO_4 (magnesium sulfate). Mix.

5.3.5 Immerse centrifuge tube into holder in centrifuge after filling holder partly with water. Centrifuge at 2500 rpm (relative centrifugal force = 1000) for 15 minutes. For many viscous oils, it may be necessary to repeat this step after removing water with pipet or to centrifuge for a longer time interval.

5.3.6 Take 1 ml of oil from the surface of the centrifuge tube with a clean pipet and place in a clean vial.

5.3.7 When running infrared spectra, make sure that there are no H_2O (2.7μ) or sulfate (SO_4^{-2}) ($8.5\text{--}9.3 \mu$) peaks.

5.4 Filling the Cell

5.4.1 Sealed Demountable Cell

5.4.1.1 Assemble clean cell with 0.1 mm Teflon spacer (always use same spacer for spectra which will be compared since spacer thicknesses may vary by $\pm 10\%$). Tighten nuts uniformly with a criss-cross sequence.

5.4.1.2 Fill the cell, tilted at 45 degrees, from the bottom port using a Pasteur pipet or syringe with a Luer-Lock tip. NOTE: Use care to avoid forming bubbles in that portion of the window which is in infrared beam.

5.4.1.3 Stopper the cell with Teflon plugs. Insert the bottom plugs first using a twisting motion. Gently insert the top plug. NOTE: If the oil is too viscous to flow in a liquid cell, smear a drop of oil in the center of the AgBr window before assembling the cell.

5.4.2 Wilks Mini-Cell

5.4.2.1 Dismantle the cell and place base and gasket on a clean Kimwipe.

5.4.2.2 Pipet one drop of oil sample into the 0.1 mm cavity of the AgBr window.

5.4.2.3 Slowly lower flat cover window onto the sample.

5.4.2.4 Inspect the window for bubbles, if present, clean the windows and repeat 5.4.2.2 using a larger drop of oil.

5.4.2.5 Insert the windows into the base and place outer threaded barrel over windows. Screw the cell together, always tightening cell in a uniform manner.

5.4.2.6 Inspect window again for bubbles.

5.4.2.7 The Wilks Mini-cell is useful especially for field use; however, it may not be sufficiently reproducible for the overlay method for similar oils using the single-beam spectrophotometer. In this case, either a sealed demountable cell or the RIIC Disposable Cell should be used.

5.4.3 RIIC Disposable Cell (Beckman) (AgCl Windows). (0.1 ± 0.002 mm pathlength.) This cell is useful for field work and has a highly reproducible path length which is important for this application; however, it can only be used on oils with relatively low viscosity because of difficulty in filling. It can be used several times by rinsing with solvent and drying by blowing air through the cell.

5.4.3.1 Fill cell using a syringe with a Luer-Lock tip (low-viscosity oils only). Plug or crimp cell shut.

5.4.3.2 Check that there are no bubbles in optical path.

5.5 Cell and Window Cleaning Procedures

For forensic work, cells and cell windows must be thoroughly cleaned. Complete removal of residual hydrocarbons is monitored by looking for a hydrocarbon peak in the 3.5 micron region. See Figure 8 for a comparison of clean and dirty cells.

5.5.1 Turn on the fan in the portable fume hood. Make sure that the exhaust hose carries fumes outside the building.

5.5.2 Use spectroquality hexane for cleaning cells used for low and medium viscosity oils. Use spectroquality toluene for cleaning cells used for very high viscosity oils such as natural seeps. NOTE: Since these solvents are very flammable, observe safety precautions. Do not smoke or use open flames in the vicinity. Avoid getting solvents on skin. Use gloves or forceps to avoid contact. Avoid breathing solvent vapor by working within hood.

5.5.3 Dismantle cell completely. Thoroughly rinse each component with spectroquality solvent. Hold windows only by the edges. Catch waste solvent in a beaker. Dispose of waste solvent immediately in safety can. Let windows air-dry on clean Kimwipes. Reassemble cell and test for absorption in 3.5μ region.

5.6 Care of Cell Windows

Silver Bromide (AgBr) and silver chloride (AgCl) windows are soft and must be handled carefully to prevent scratching. It is important to protect them from light as much as possible, since they darken on exposure to ultraviolet light. Check spectra of empty cell frequently to see if the spectral baseline had changed enough ($> 5\%$ Transmission at 7.5μ) to warrant replacement of windows. Silver bromide (and chloride) reacts with certain base metals (such as aluminum, zinc, brass, copper and iron) especially at higher temperatures and in the presence of moisture. Although no reaction has been observed with stainless steel and/or lead, as a precaution, do not leave the cell assembled for prolonged periods of time. Dismantle cell, dry windows and wrap them in lens paper before storing.

6.0 CONCLUSIONS AND SUMMARY

A preliminary survey of instrumental methods (not described here) indicated that the Miran (single-beam) infrared spectrophotometer was the simplest and most economical means to distinguish natural seeps from similar production oils in the Santa Barbara, California region. This method involves simple, low-cost infrared instrumentation and requires a minimum of sample preparation. It permits rapid on-site analyses without extensive training.

A survey of production oils from the Santa Barbara off-shore drilling platforms indicated that the brown zone (Dos Cuadras) oil was the most similar to the natural seeps in infrared spectra (and chemical composition). Therefore, this brown zone oil was selected as the most suitable for a test of the experimental method.

The major differences between seep and non-seep oils appear in the comparison between the 13.8μ and 13.5μ peaks (for both weathered and unweathered oils) and in the carbonyl region at 5.85μ (for unweathered oil only). The $13.5 \mu / 13.8 \mu$ peak ratio gives a rough indication of the relative aromatic/aliphatic content of the oil and the natural seeps have the most aromatic character of all oils tested. Differences between seep and non-seep oils based on this peak ratio have been found to persist in weathering studies for at least one week.

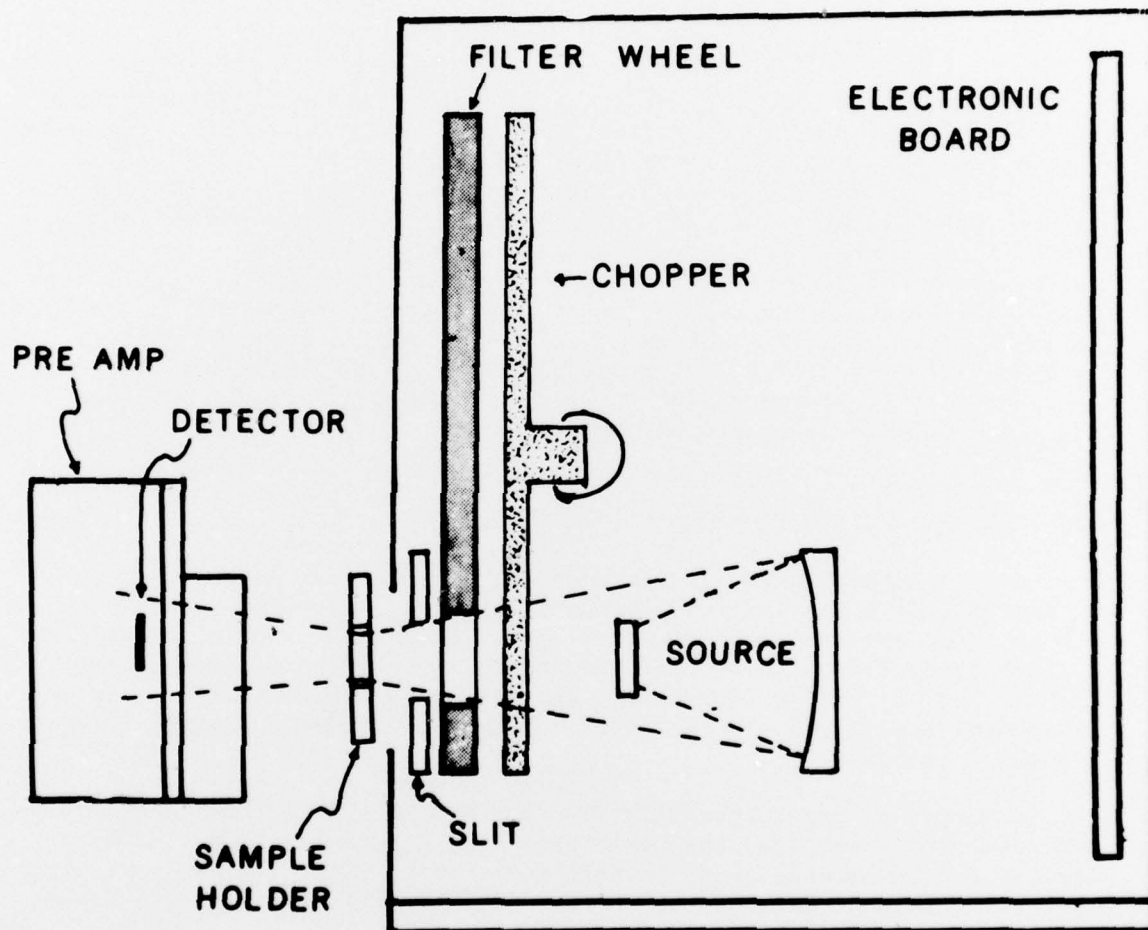


FIGURE 1. DIAGRAM OF MIRAN I INFRARED ANALYZER.

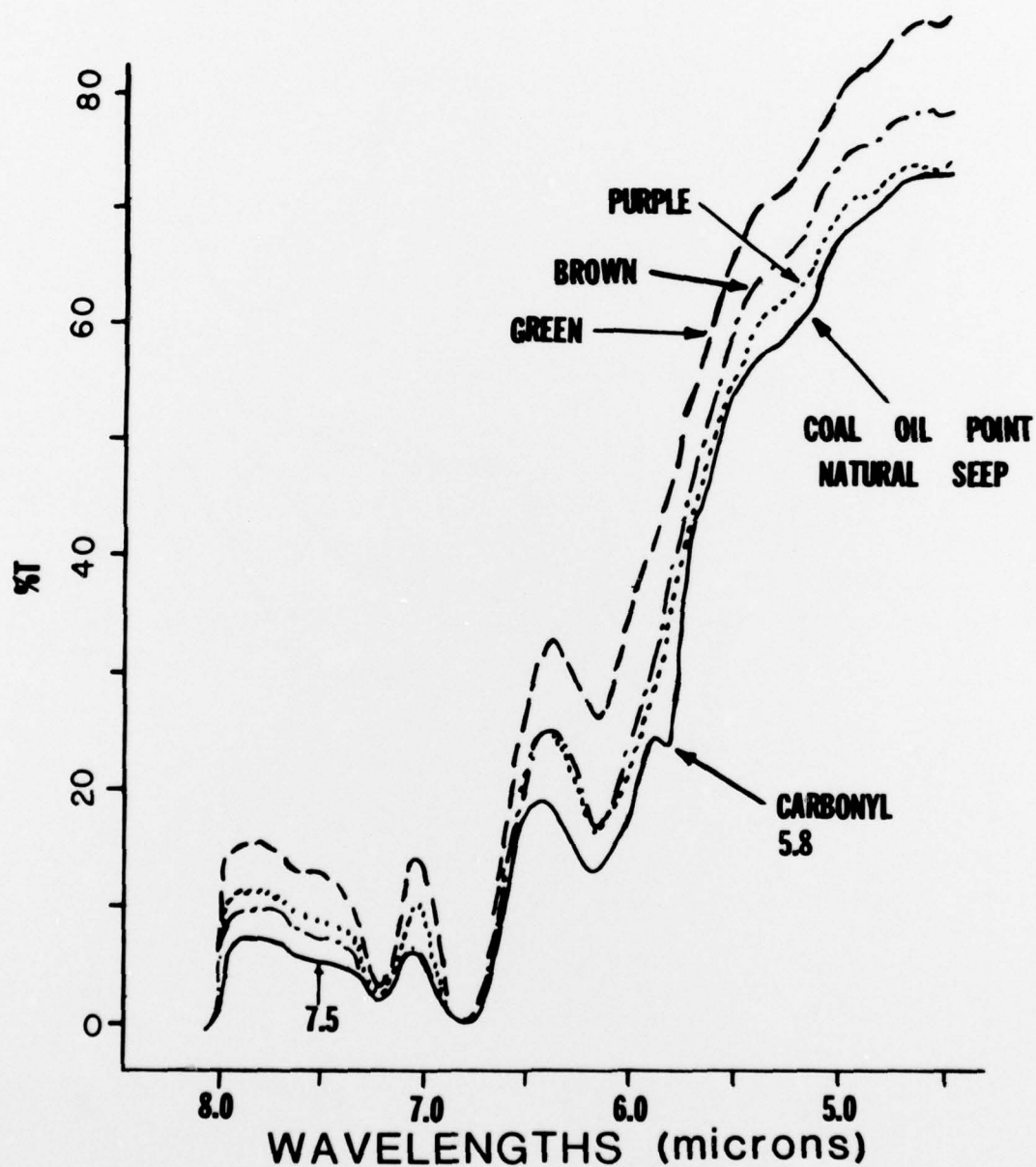


FIGURE 2. DIFFERENCES IN MIRAN SPECTRA-SANTA BARBARA CRUDE OILS (TRANSMITTANCE SCALE).

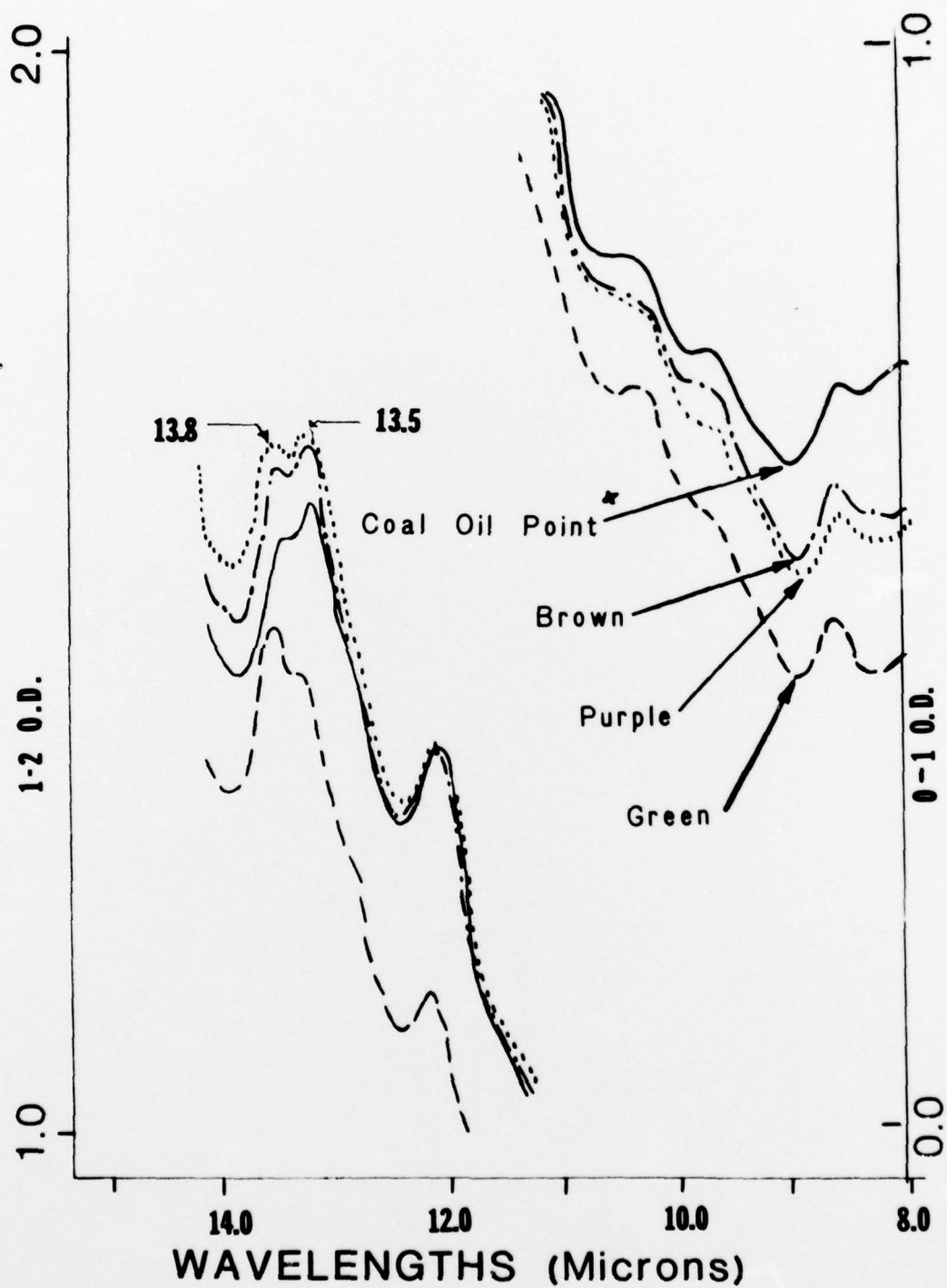


FIGURE 3. COMPARISON - NATURAL SEEP VS. PRODUCTION OILS (ABSORBANCE SCALES).

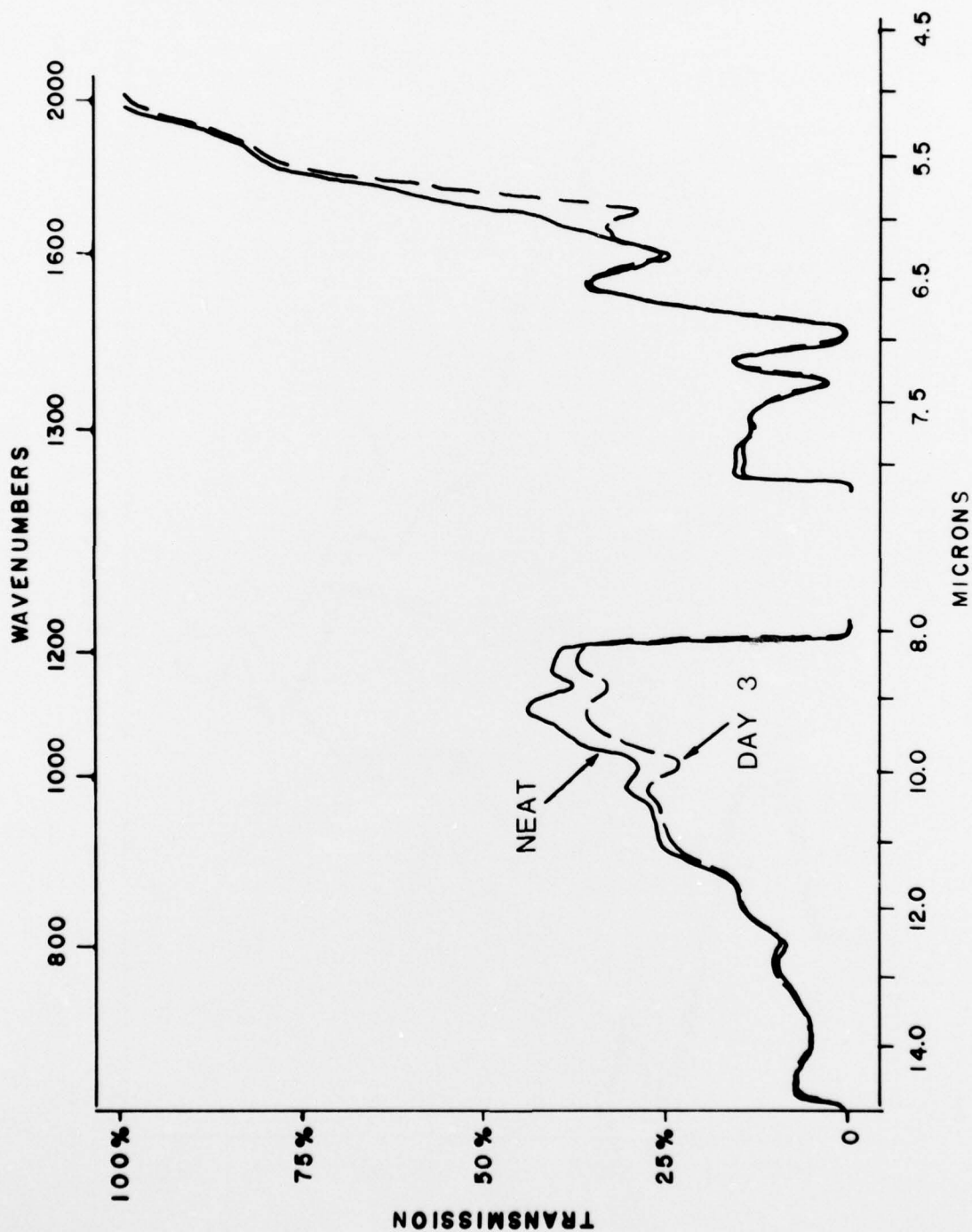


FIGURE 4. WEATHERING COMPARISON - BROWN (DOS CUADRAS) OIL -
NEAT VS. DAY 3 (TRANSMITTANCE SCALE).

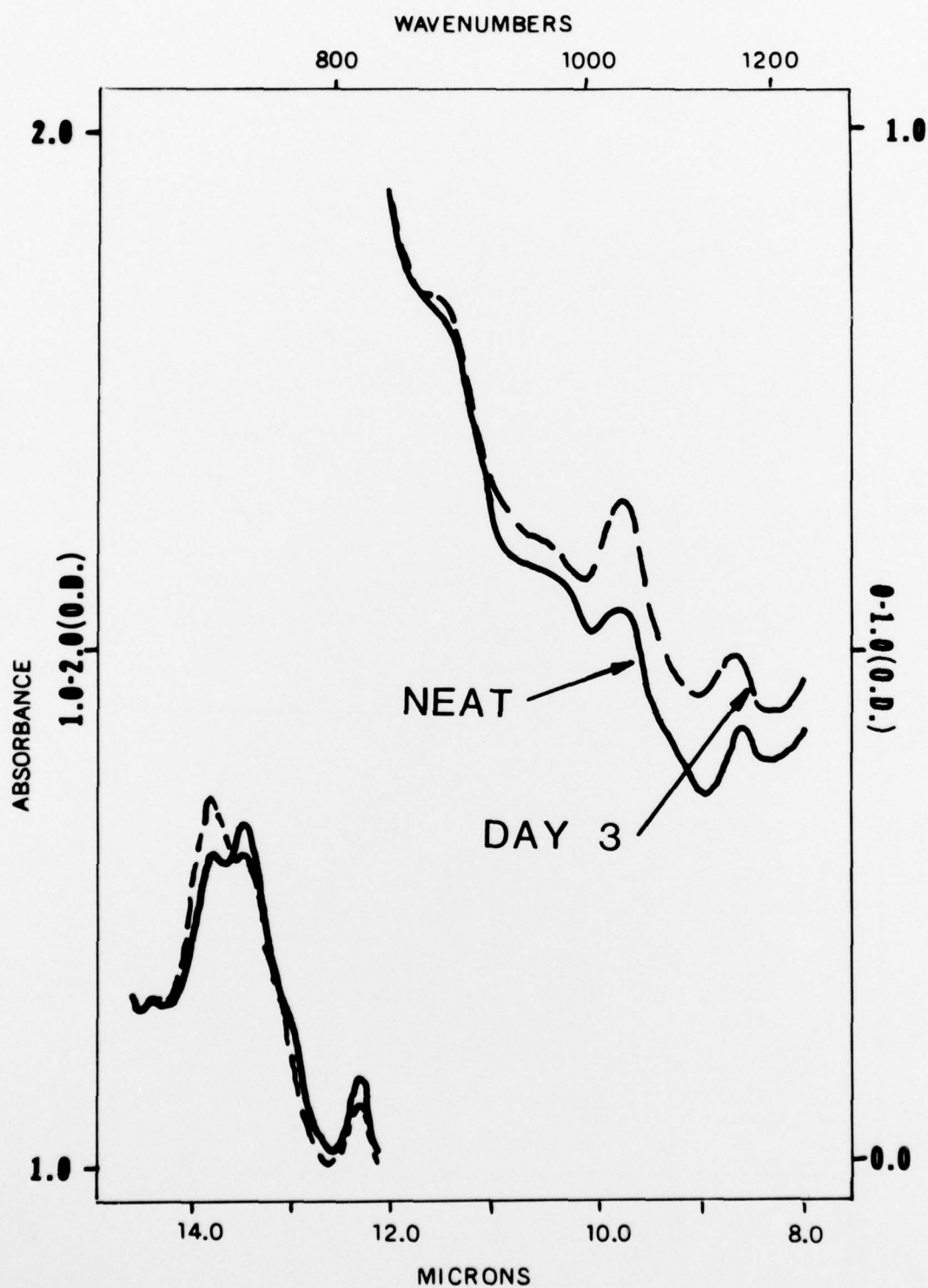


FIGURE 5. WEATHERING COMPARISON - BROWN (DOS CUADRAS)
OIL - NEAT VS. DAY 3 (ABSORBANCE SCALES).

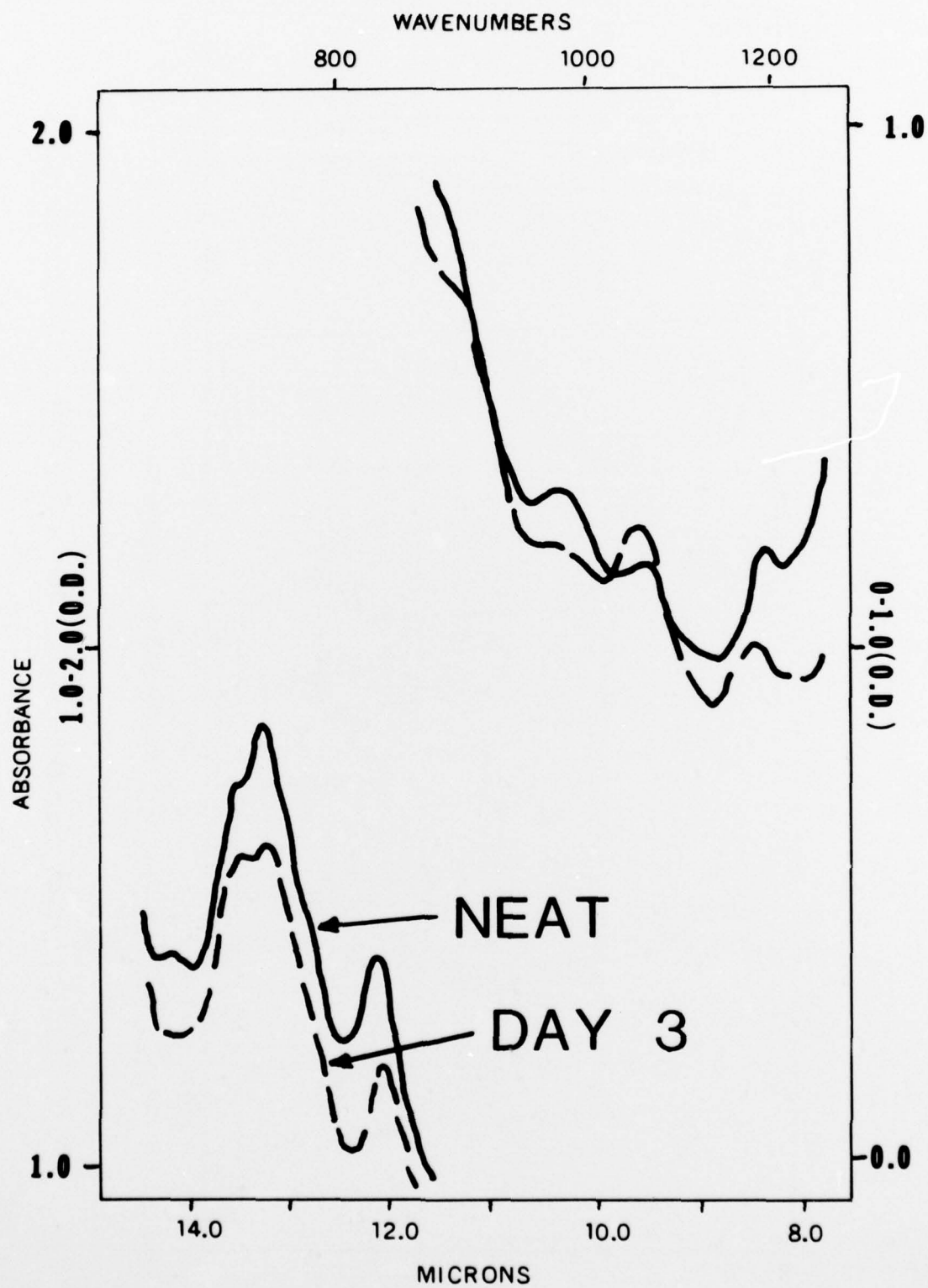


FIGURE 6. WEATHERING COMPARISON - NATURAL SEEP OIL - NEAT VS. DAY 3 (ABSORBANCE SCALES).

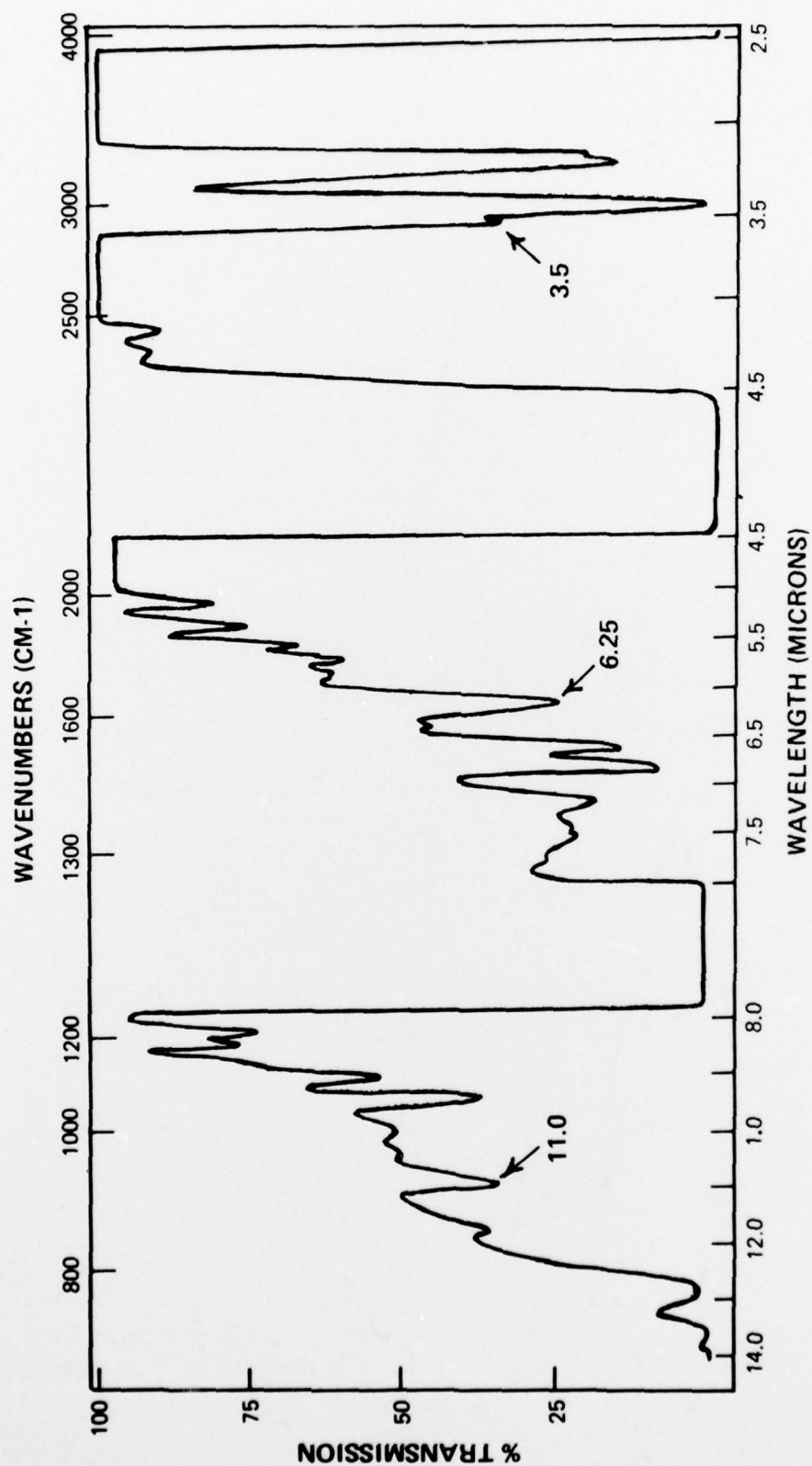


FIGURE 7. MIRAN INFRARED SPECTRUM OF POLYSTYRENE FILM (TRANSMITTANCE SCALE).

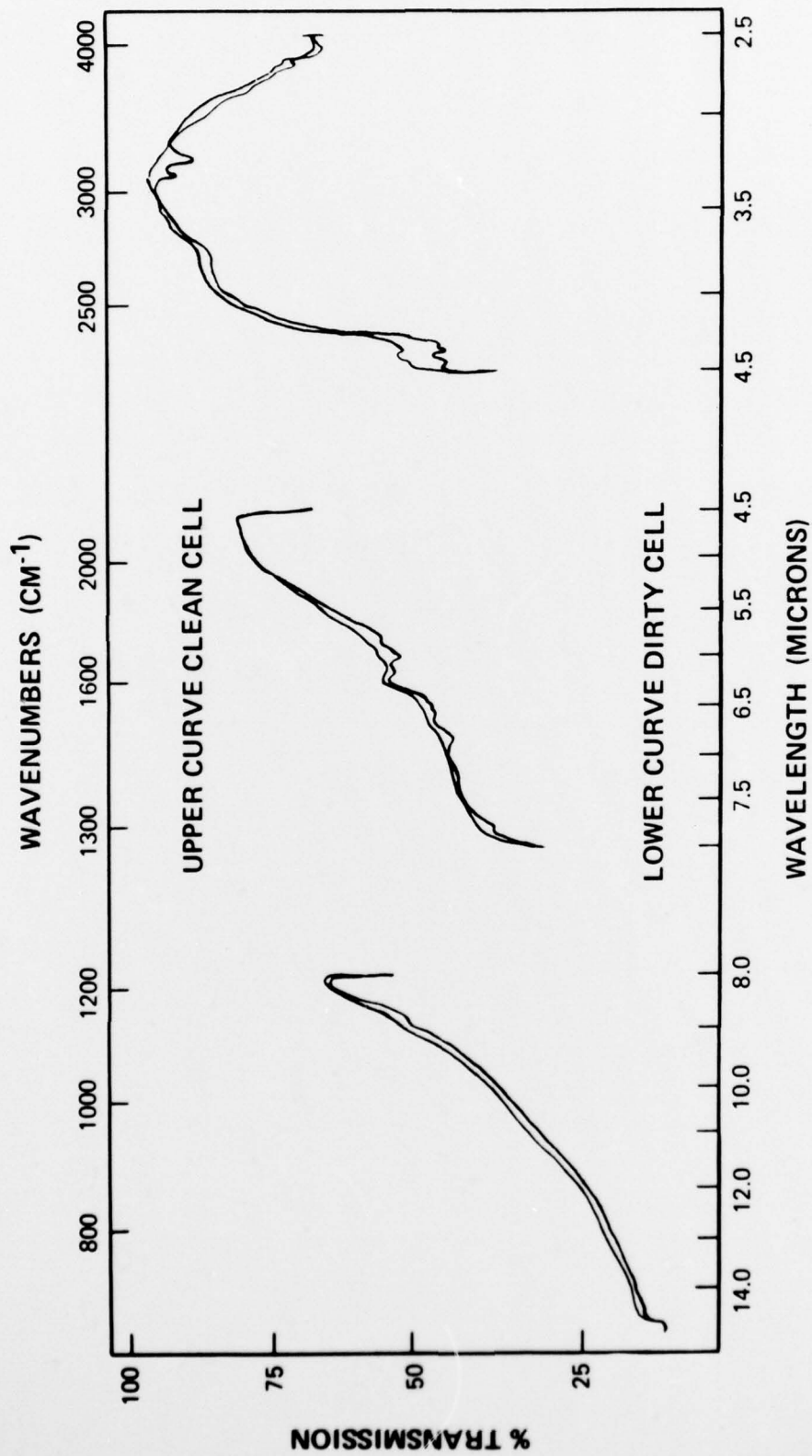


FIGURE 8. MIRAN INFRARED SPECTRA COMPARING CLEAN AND DIRTY CELLS (TRANSMITTANCE SCALE).

TABLE 1. SPECIFICATIONS OF VARIABLE
FILTER MIRAN I (MODEL 5649).

WAVELENGTH RANGE	2.5 TO 14.5μ IN 3 STEPS
RESOLUTION (SLIT 0.5)	0.05μ @ 3μ 0.25μ @ 11μ
NOISE LEVEL	S/N = 10^4 , NO CELL, 1 MM SLIT 1 SEC TC AT 3.5μ (23°C)
DRIFT	$\pm 1\%/24$ HRS ($<1\%$ NOISE)
PHOTOMETRIC ACCURACY	$>0.5\%$